# X. ALH 84001

Orthopyroxenite, 1931 grams Weathering A/B, Fracturing B



Figure X-1. Photograph of exterior surface of Martian meteorite ALH84001. The cube is 1 cm. (NASA # S85-39570)

#### Introduction

ALH84001 was found during a snowmobile ride December 27th, 1984 in the Far Western Icefield of Allan Hills and was picked up (as sample number 1539) without the usual careful photography. The ANSMET Field Notes describe it as a "highly-shocked, grayish-green, achondrite, 90% covered with fusion crust (with the additional comment 'Yowza-Yowza')." Since it was recognized as the most unusual rock collected, it was the first Antarctic meteorite to be processed from the 1984-5 field season (Score, 1997).

The fusion crust has spalled in some areas from the hackly end (W1), exposing a uniform coarse-grained rock with a greenish-gray color and a blocky texture

(figures X-1, X-2) (Score and MacPherson, 1985). During preliminary examination, Mason *et al.* (1992) noted cleavage planes on some large crystals and that the stone had a "shocked appearance." ALH84001 was originally classified as a diogenite by Score and MacPherson (1985) and Mason *et al.* (1992), although they noted "patches of brown Fe-rich carbonate." Preliminary examination classified ALH84001 as weathering category A/B and fracturing category B (moderate cracks).

However, during a study of diogenites, Berkley and Boynton (1992) and Mittlefehldt (1994a) noted that

<sup>\*</sup>The sample described by Sack *et al.* (1991) was not *bona fide* ALH84001, rather it was a mislabeled sample of the EETA79002 diogenite (Score and Lindstrom, 1993).



**Figure X-2.** Photograph of exterior surface of Martian meteorite ALH84001. The cube is 1 cm. (NASA # S85-39567)

the chromite in ALH84001 contained substantial Fe<sup>+3</sup>. Mittlefehldt also noted that the rock contained pyrite rather than troilite and had unusual Fe/Mn for a diogenite. Finally, based on oxygen isotope analysis of Clayton (1993b), ALH84001 was reclassified as a Martian meteorite (Score and Mittlefehldt, 1993).

As explained below, this Martian meteorite has been found to have a very old age (~ 4.5 to 4.0 Ga), but it has suffered several impact events during its history, as evidenced by annealed granular bands and isotropic plagioclase, making age determinations difficult to interpret. This sample also has the oldest cosmic-ray, exposure age (~15 Ma) of the 12 known Martian meteorites (figure I-11).

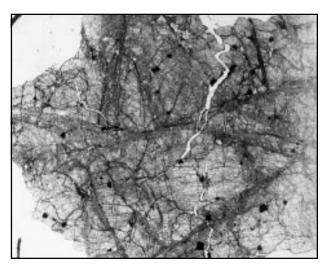
A most unusual feature of this rock is the presence of rare, small (100-200 microns), fine-grained, spheroidal



Figure X-3. Close-up photograph of interior surface of a small piece of Martian meteorite ALH84001 illustrating rounded carbonate inclusions (orangettes). The interiors are orange and the rims are black-white-black. The size of the orangettes is 100-200 microns. (NASA # S95-00690) - provided to NASA by Monica Grady. This figure was originally published in color in Nature 372, 616.

areas of zoned Mg-Fe-Ca carbonate (figure X-3). Thomas *et al.*, 1995, 1996 and Romanek *et al.*, 1995 proposed that organic matter and small magnetite grains associated with the outer rims of these carbonate spheroids may have a biological origin. In August 1996, McKay *and eight co-authors* published their evidence of past biological activity on Mars preserved within the outermost black rims of the carbonate globules of this sample (*see section on "Biogenic Hypothesis" below*). Consequently, NASA was apparently asked to "put its full intellectual power and technological prowess behind the search for further evidence of life on Mars" (Kerr, 1996).

Recent review papers by McSween (1997), Gibson et al. (1997), Gleason et al. (1997) and/or Treiman



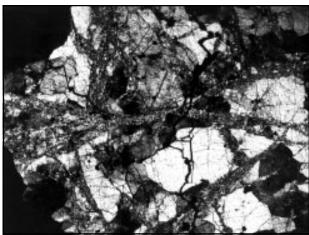


Figure X-4. Photomicrographs of thin section of ALH84001,64 (plane polarized and cross polarized light). Field of view is about 6 mm. These figures are figures 1a and b from Mittlefehldt 1994, Meteoritics 29, 215. They illustrate the crushed zones within the coarse orthopyroxene grains. Figures kindly provided by Duck Mittlefehldt.

(1998) should give the reader a framework for what follows.

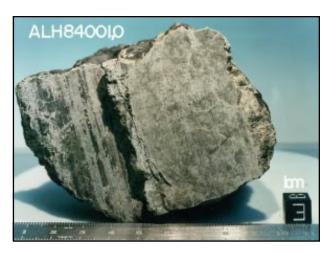
# **Petrography**

ALH84001 is a coarse-grained, cataclastic orthopyroxenite (97% orthopyroxene, 2% chromite, ~1% maskelynite, 0.15% phosphate) with minor augite, olivine, pyrite and secondary Fe-Mg-Ca carbonate. The igneous minerals are essentially unzoned whereas the carbonate is highly zoned in composition. Mason et al. (1992) described a thin section with "orthopyroxene crystals up to 5 mm long forming a polygonal-granular mosaic" (figures X-4a and b). Berkley and Boynton (1992) reported orthopyroxene grains up to 6 mm, which commonly join in 120° triple junctions (Mittlefehldt, 1994a). Chromite is found as euhedral inclusions in the orthopyroxene. Minor maskelynite and chromite are found at the interstices.

A macroscopic description of hand specimen ALH84001,65 by Mittlefehldt (1997) revealed that granular bands within the orthopyroxenite were cut by old, pre-terrestrial fractures. The granular bands can be distinguished by (1) deformed chromites, often forming stringers, (2) streaks of light and dark silicates, and (3) a sugary texture. These bands are roughly planar, but there is no preferred orientation. Mittlefehldt also observed that old fracture surfaces cross-cut granular bands and noted that these old fracture surfaces are distinguishable by, (1) transecting more than one pyroxene grain, (2) a general gently



**Figure X-5.** Photograph of sawn surface of Martian meteorite ALH84001,65 illustrating the porosity of the interior of the sample. The cube is 1 cm. (NASA # S94-32547)



**Figure X-6.** Photograph of sawn surface of Martian meteorite ALH84001,1 after the second saw cut illustrating the porous "crushed" zone in the middle of the sample where the break occurred during sawing. (NASA # S94-32548)

undulating shape, (3) a waxy appearance, and (4) a fine-scale, wavy structure similar to 'slickensides' in appearance. Thin, round to elliptical, disks of colorzoned carbonate were found to be prevalent along the old fractures. From these observations Mittlefehldt concluded that the sequence was, (1) formation of the granular bands, (2) formation of the old fracture surfaces, and (3) deposition of the rounded, zoned carbonate blebs.

Thin sections of ALH84001 contain mm-wide bands of crushed and annealed orthopyroxene with a fine granular texture and grain size 10-30 microns (Treiman, 1995b). The offset along these granular bands is indicated by the length of sheared chromites (several 100 microns).

Photographs of the large sawn surface through the center of ALH84001 (figures X-5, X-6) reveal a centimeter-wide light-colored zone in the center of the rock that has become known (for allocation purposes) as the "crushed zone". Photos of this centimeter-wide band show that it has ~5-10 % elongate cavities (possibly interconnecting). Thomas et al. (1995) illustrate a SEM photo of an interior surface of a cavity in this band. Gleason et al. (1997) found a slight difference in the trace element composition of this "zone" (figure X-25). However, Mittlefehldt (personal communication) found nothing unusual about the appearance of this region of the rock in his examination of the hand specimen (1997).

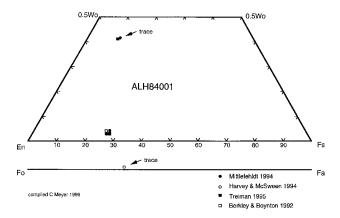


Figure X-7. Compositional diagram for pyroxene in ALH84001. Only trace olivine and augite are present. Most of the rock is orthopyroxene. Data replotted from Berkley and Boynton (1992); Mittlefehldt (1994); Harvey and Treiman (1994); and Treiman (1995).

Away from this central zone, the porosity of the main part of the rock is only 1-2% and apparently non-penetrating. A few mm-size vesicles or voids can readily be seen in the photos of the sawn surface (figures X-5, X-6).

The presence of small patches of carbonates along annealed fractures in ALH84001 has led to numerous studies. In thin section, some of these carbonates appear to be replacing maskelynite (Treiman, 1995b). An important debate has been whether these carbonates formed at high or low temperature (Harvey and McSween, 1996; McKay *et al.*, 1996; Valley *et al.*, 1997). Mittlefehldt and Lindstrom (1994a), Wadhwa and Crozaz (1994c, 1995b), Treiman (1995b) and Griffith and Shock (1995) have addressed the issue of apparent metasomatism that must have accompanied the CO<sub>2</sub> alteration of this rock (*see the section on "Carbonate Orangettes"*).

In summary, detailed petrography of thin sections of ALH84001 shows that, after cooling in an igneous plutonic environment, ALH84001 was subjected to at least two shock events as well as alteration in a CO<sub>2</sub>-rich fluid (Mittlefehldt, 1994a; Treiman, 1995b; Gleason et al., 1997; McKay et al., 1998; Treiman, 1998). However, Scott et al. (1997a, b) concluded only one shock event is evident in the sample studied by them (,53) and pointed out that, a sequence of events can occur in an instant (geologically speaking) during and immediately after an impact event. However, it seems clear that this rock has had a long and varied history (since about 4.5 Ga) on the surface of an active planet (Mars) (see below).

SEM studies by Wentworth and Gooding (1995) and Wentworth *et al.* (1998) found that the fusion crust of ALH84001 is extremely fresh and unaltered, *although preliminary examination assigned the sample weathering category A/B*. From the density of nuclear tracks, Goswami *et al.* (1997) have concluded that the outer 5 centimeters was ablated away during entry into the Earth's atmosphere.

### **Mineral Chemistry**

Orthopyroxene: Mason et al. (1992) reported orthopyroxene crystals up to 5 mm long. The orthopyroxene in ALH84001 (figure X-7) is homogeneous in composition (Wo<sub>3</sub>Fs<sub>27</sub>) and no pyroxene exsolution lamellae were observed (Berkley and Boynton, 1992; Mittlefehldt, 1994a; Treiman, 1995b). Papike et al. (1994) and Wadhwa and Crozaz (1994) have determined the REE in the orthopyroxene and calculated the composition of magma that would be in equilibrium. However, Treiman (1996a) argued that it is not possible to calculate the composition of the original magma using equilibrium partition coefficients, if the sample has undergone subsolidus equilibration.

*Olivine*: Minor olivine (Fa<sub>34.5</sub>) has been reported (Harvey and McSween, 1994; Shearer and Leshin, 1998; Shearer and Adcock, 1998) as minute inclusions in orthopyroxene. Harvey and McSween (1996) also reported trace olivine in the crushed zones. *Note that the olivine reported by Sack et al.* (1991) is of a mislabeled sample.

*Maskelynite*: Mason *et al.* (1992), Berkley and Boynton (1992) and Mittlefehldt (1994a) determined the composition of the maskelynite to be An<sub>35-39</sub>Or<sub>3-4</sub>.

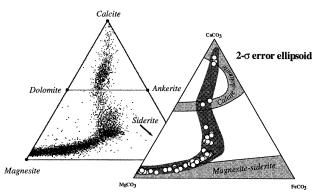


Figure X-8. Composition diagram for carbonates in Martian meteorite ALH84001. This is figure 2 in Harvey and McSween 1994 and figure 3 in Harvey and McSween (1996), Nature 382, 51.

Mittlefehldt found that some maskelynite analyses had excess Si, inferring that the original plagioclase may have been intergrown with SiO<sub>2</sub>. Wadhwa and Crozaz (1994) determined the REE abundance in maskelynite. However, Scott *et al.* (1997a, b) found that the "maskelynite" in this sample is rather "plagioclase glass". Greenwood and McSween (1998) reported analyses of "mixed feldspar glass" and "mobilized plagioclase glass" as well as stoichiometric maskelynite. Brearley (1998), Treiman and Treado (1998) and Shearer and Adcock (1998) also report on the composition and distribution of shocked feldspar glass in ALH84001.

**K-feldspar**: Turner *et al.* (1997) and Greenwood and McSween (1998) reported the composition of "orthoclase glass" (~ Or <sub>52</sub>).

**Chromite:** Euhedral grains of chromite occur as inclusions in the orthopyroxene and in the interstices. Some chromite is found as "schlieren" in the sheared, granular zones. Berkley and Boynton (1992), Mittlefehldt (1994a) and Gleason *et al.* (1997) documented the presence of significant Fe<sup>13</sup> in chromite. The Fe<sub>2</sub>O<sub>3</sub> content of ALH84001 chromite measure  $\sim 5.3$  wt. % based on 6 analyses by Berkley and Boynton (1992) and 7.7 wt. % based on 103 analyses by Mittlefehldt (1994).

**Phosphates:** Minor apatite (~300 microns) occurs as interstitial grains (Wadhwa and Crozaz, 1994, 1995b; Mittlefehldt, 1994a). Large grains of whitlockite (up to 800 microns) have been analyzed by Boctor *et al.* (1998a,b) for D/H. Cooney *et al.* (1998) obtained infrared reflectance spectra of chloroapatite and merrillite.

Carbonates: (see also section on "Carbonate Orangettes" below) According to Romanek et al., (1994a, 1995) about 1% of ALH84001 is orange-colored carbonate, however, the carbonate is heterogenously distributed and the amount of carbonate in the rock as a whole appears to be very minor and may actually be considerably less than 1% (Dreibus et al., 1994 estimated 0.46%). However, cursory examination of all of the thin sections of ALH84001 by Chuck Meyer, showed that at least some carbonate was present in every section.

Carbonate in ALH84001 occurs in several habits (McKay et al., 1997; Scott and Krot, 1998). Some carbonate is found as an interstitial filling in cracks (Mason et al., 1992). Some is found as interstitial carbonate clusters (~100-200 microns in size) usually associated with maskelynite (possibly as 'replacement' of maskelynite (Treiman, 1995b) and/or orthopyroxene (Mittlefehldt, 1994a). These carbonate clusters are zoned, from Ca- and Fe-rich to Mg-rich (Harvey and McSween, 1995, 1996; McKay and Lofgren, 1997; Scott et al., 1997; Gleason et al., 1997). Zoning is oscillatory, with two pronounced black zones (Fe-rich) sandwiching a white Mg-rich zone, indicating that precipitation was not from a single event. These carbonate grains appear to pre-date the last shock event as evidenced by offset fractures (Mittlefehldt, 1994a). Harvey and McSween (1995, 1996) and Treiman (1995b) report analyses of the carbonate "rosettes" (figure X-8). Mason et al. (1992) and others reported the average analysis of the carbonate as (Fe<sub>30</sub>Mg<sub>60</sub>Ca<sub>11</sub>)CO<sub>3</sub>. Romanek et al. (1995) describe the carbonates as "spheroidal aggregates or finegrained vug-filling structures." Another occurrence is as "thin pancakes" found attached to broken surfaces (McKay et al., 1996).

The carbonate "orangettes" also exhibit considerable Mn/Fe zonation. McKay et al. (1996) reported an inner core of Mn-enriched, Ca-carbonate in one "orangette" (see also analyses for Mn by Treiman, 1995b). Further details of the carbonate zonation are reported by McKay and Lofgren (1997), Scott et al. (1997), Gleason et al. (1997). McKay et al. (1998) discuss narrow cracks filled with carbonate, where the zonation across the crack is similar to that in the globules, and presumably of the same generation.

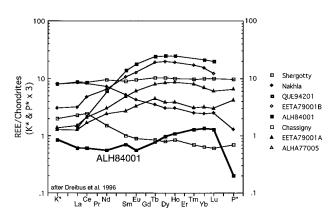


Figure X-9. Normalized rare earth element diagram for Martian meteorites with ALH84001 marked as heavy line. This figure is modified from Dreibus et al. (1996).

<sup>\*</sup>Mittlefehldt (1994c) corrected his earlier reported value for K.

Table X-1. Chemical Composition of ALH84001.

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									(e)	રે												<b>e</b>	e e	(e) (e)					(e)	@ @ @	<b>9 9 9</b> 3
Dreibus94	71 mg								0.024	1000												0.83	1.63	5.89					0.04	0.15	0.06 0.265 0.104
_					(a)	(a)	(g)	(a)	(a)					(a)	(0)	a) (e	(a)	(a)	(a)	3	(a) (a)									(a)	(a)
Dreibus94	236 mg				17.6	0.443	7:1	0.162	0.022					12.7	0400	8498 43	<20	106	3.2	000	<0.08									0.13	0.1
Dreibus94 Dreibus94	52.7 mg		52.7 (d)		(p)	5	1.62 (d) 24.5 (d)	)	0.026 (d)	98.1	580 (f)		110 (f)																		
Mittlefehldt94	251mg	,20			17 (a)		2 (a)	0.0867(a)	0.013*(c)					12.4 (a)	(2) (7)	0842 (a) 46.3 (a)														0.158(a)	0.107 (a)
Warren 96																	5.8 (b)	(b) 67		1.08 (b)						į.	(9)				
Warren 96			52.84 0.2	1.21	17.24	0.47	24.7	0.135	0.015	98.63				11.8 (a)	205 (a)	/300 (a) 44.6 (a)	<12 (a)	82 (a)	2.74 (a)	(7)3000	<0.025(a) <0.163(a)									0.246 (a) 0.65 (a)	0.16 (a)
Warren 97	332 mg	485,	52.93 0.2	1.21	17.36	0.47	1.61	0.151	0.015	98.85				13.1	205	8000 50	<20	92	2.3		<0.23	8.7.8	<del>4</del> 7>	<38					<0.05	0.28 0.7	<0.9 0.163
Warren 97	337 mg	,58a	52.93 0.7	1.21	17.23	0.47	1.62 24.7	0.145	0.015	98.72				11.8	205	/300 45	5.8	06	2.74	1.08	<0.17					ŗ				0.246 0.65	0.16
Gleason 97			50.3	1.38 (a)	18.4 (a)	0.455 (a)	1.77 (a) 26 1 (a)	0.132 (a)	0.015 (a)	72.86				13.0 (a)	197 (a) 8140 (a)	8140 (a) 48.9 (a)		91.6 (a)	3.24 (a)										0.045 (a)	0.185 (a)	0.114 (a)
	weight	split	SiO2 % TiO <i>2</i>	A1203	FeO	MnO	Ç X	Na20	K20	uns	Li ppm C	) <u>L</u> .	s 5	S S	> Ċ	පි පි	ïZ	3 5	Ga	g •	Se	R &	አ	Z, N	Mo Pd ppb	Ag ppb	odd m In ppb Sb ppb	Te ppb	Cs ppm	c ra	Pr Sm d

			0.2152(g)		44.49 (g)							
<b>@ @ @</b> (	© © ©	<u>e</u> e	(e)								(e)	(e)
0.14 0.03 0.24	0.068 0.21 0.036	0.255 $0.037$	0.16								0.035	0.01
(a) (a)	(a)	(a) (a)	(a)	(a)				(a)	(a)		(a)	(a)
0.04	0.0/	$0.31 \\ 0.051$	0.17	<0.04				Q	1		<0.06	0.012
0.036(a)		0.27 (a) 0.045 (a)	0.12 (a)			0.00166(b)	0.0102(b)	0.08 (b)	0.0094(b)			
0.043 (a)		0.262 (a) 0.042 (a)	0.117 (a)	<0.042(a)						<0.047 (a)	<0.047 (a)	
0.042	0.07	0.3 0.050	0.111	<0.06				<2.2	<0.640		0.11	<0.03
0.043		0.262 0.042	0.117	<0.042		0.00166	0.0102	80.0	0.0094		<0.05	<0.3
0.039 (a) 0.31 (a)	0.081 (a)	0.317 (a) 0.053 (a)	0.18 (a)	0.032 (a)	79 (a)							
g 12 d	Ho Th	r. Lr	Æ	Та	W ppb	Re ppp	Os ppb	Ir ppb	Au ppb	Tl ppb Bi ppb	Th ppm	U ppm

technique (a) INAA, (b) RNAA, (c) Mittlefehldt 94b, (d) XRF, (e) spark source mass spec. (f) carbon-sulfur analyzer, (g) IDMS

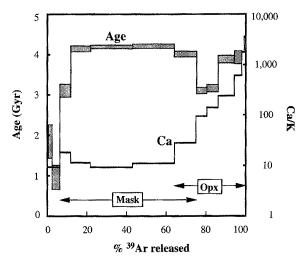


Figure X-10. Ar plateau diagram for ALH84001,100. While a simple plateau age is 4.1 to 4.2 Gyr, the "best overall age is obtained from the total argon released over 400°C," giving an age from 3.9 to 4.1 Gyr. This is figure 2 from Ash et al. (1996), Nature 380, 58.

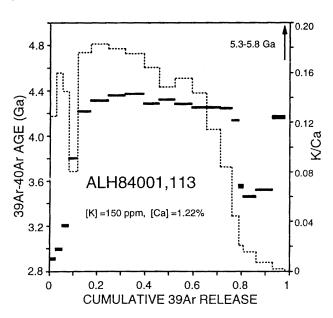


Figure X-10b. Ar plateau diagram for ALH84001,13. This figure is from Bogard and Garrison (1997), Early Mars Workshop.

Wadhwa and Crozaz (1995b) have reported the REE contents for carbonates (figure X-27).

*Silica*: Silica (phase unknown) has been reported in the centers of some of the carbonate areas where the magnesite rims come together (Harvey and McSween, 1995, 1996). Original igneous silica-plagioclase intergrowth is also inferred from Si-rich maskelynite analysis (Mittlefehldt, 1994a). Silica patches in orthopyroxene were reported by Valley *et al.* (1997),

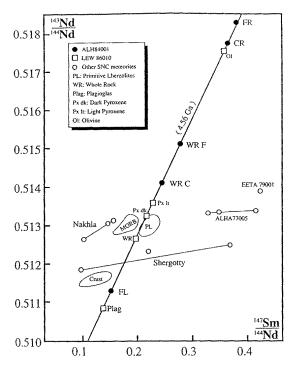


Figure X-11. Sm-Nd isochron diagram for mineral separates and whole rock samples from Martian meteorites including ALH84001. This is figure 3 from an abstract by Jagoutz et al. (1994), Meteoritics 29, 479.

Scott *et al.* (1997) and Turner *et al.* (1997). Valley *et al.* also studied a thin "silica vein" cutting across *a* "*carbonate concretion.*"

Westall *et al.* (1998) describe an amorphous silica coating on the internal surfaces where the carbonate globules are found. They find that this silica film postdates the secondary fracturing of the carbonate globules and is evidence that "low-temperature, silicarich, hydrothermal fluids" percolated through the rock. McKay *et al.* (1998) describe a set of very fine, "weblike" veins of low Z material occupying the intersitices between angular or slightly rounded fragments of feldspar and also conclude this is evidence for fluid transport and deposition.

Sulfides: Pyrite grains ~10 microns have been reported associated with interstitial chromite, maskelynite and/or carbonate "orangettes" by Mittlefehldt (1994a) and Treiman (1995b). Extremely fine-grained sulfides (~100 nm) are found in the black rims on the carbonate clusters (McKay et al., 1996). Some of the fine-grained sulfide is identified as pyrrhotite and some is tentatively identified as "greigite" (McKay et al., 1996). Wentworth and Gooding (1995) reported minute, delicate, feathery grains of ZnS within the carbonate clusters. Shearer

et al. (1996a, b), Greenwood et al. (1997a, b) and Boctor et al. (1998) have reported isotopic data for sulfur for some of the larger grains of pyrite.

**Augite:** Minor augite (Wo<sub>42</sub>Fs<sub>12</sub>) has been reported by Treiman (1995b) (figure X-8). It is found in interstitial regions associated with maskelynite and apatite.

Glasses: Thomas et al. (1996) reported three types of glass: 1) maskelynite, 2) melted orthopyroxene and 3) SiO<sub>2</sub>. McKay and Lofgren (1997), Scott et al. (1997) and Greenwood and McSween (1998) reported "plagioclase glass". Brearley (1998) and others have observed that feldspathic glass was remelted and remobilized after formation of the carbonate.

Magnetite: Fine-grained magnetite (~10-75 nm) has been reported in the Fe-rich rims of the carbonate spheroids (Thomas et al., 1996; McKay et al., 1996; Golden et al., 1997; Thomas-Keprta et al., 1998)(figure X-23). McKay et al. claim that these small magnetite grains "did not contain detectable amounts of minor elements" and that they "are single-domain crystals having no structural defects." However, Bradley et al. (1996, 1997, 1998) found that the morphologies and defect structures of magnetite grains that they studied "are inconsistent with a biogenic origin." They report whiskers of magnetite and nanocrystals of magnetite that are epitaxially intergrown with one another and the carbonate substrate upon which they are deposited. Magnetite as a product of biomineralization is reviewed by Chang and Kirschvink (1989).

Blake *et al.* (1998) also report epitaxial or nearepitaxial orientation of magnetite with host carbonate

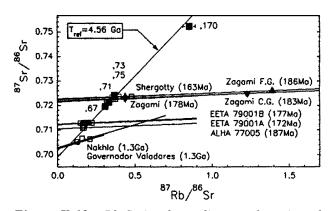


Figure X-12. Rb-Sr isochron diagram for mineral separates and whole rock samples from Martian meteorites including ALH84001. This is figure 1 from an abstract by Nyquist et al. (1995), LPSXXVI, 1065.

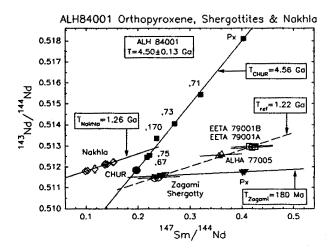


Figure X-13. Sm-Nd isochron diagram for mineral separates and whole rock samples from Martian meteorites including ALH84001. This is figure 2 from an abstract by Nyquist et al. (1995), LPSXXVI, 1066.

which is suggestive of an inorganic origin. Brearley (1998) propose an origin of fine grain magnetite in ALH84001 by partial thermal decomposition of siderite.

Compiler's note: Hey, that's consistent with where it is found!

Absence of hydrous silicates (?): The apparent absence of hydrous silicates in this meteorite was initially noted by several researchers (Mittlefehldt, 1994a; Harvey and McSween, 1994; Treiman, 1995b and Wentworth and Gooding, 1995). However, Thomas-Keprta et al. (1997) and Wentworth et al. (1998) reported "individual packets (nm-sized) and relatively large regions (~400 x 500 nm in size) of phyllosilicates in the orthopyroxene regions found near some carbonate globules. The basal spacings

measure 10-11 A suggesting this is a smectite-type clay". So far, this is the only documented report of hydrated minerals in ALH84001. It should be noted that hydrous silicates should be abundant, if the carbonates in this rock are the product of "hydrothermal" reaction (Griffith and Shock, 1995, 1997).

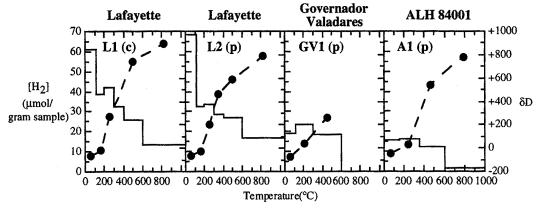
Salts: Wentworth and Gooding (1995) and Wentworth et al. (1998) reported trace amounts of Fe-sulfate, a possibly hydrated form of Mg-carbonate, patches of amorphous silica with micron-sized grains of NaCl and a single Ca-sulfate crystal. They found that the fusion crust of ALH84001 is among the least weathered of any Antarctic meteorites.

### **Whole-rock Composition**

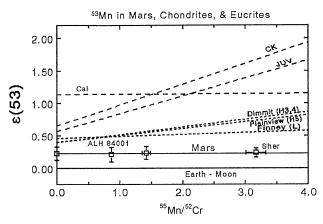
Dreibus *et al.* (1994), Gleason *et al.* (1997) and Warren and Kallemeyn (1996, 1997) give complete analyses of ALH84001 (table X-1). ALH84001 is a very mafic rock with high Mg/Fe ratio. Mittlefehldt (1994a) also reported INAA analysis of ALH84001 (figure X-9). Dreibus *et al.* noted the relatively high concentration of "volatile" elements (particularly Zn = 106 ppm). However, Jovanovic and Reed (1987) reported only 14 ppb Hg.

Warren and Kallemeyn (1996) and Ebihara *et al.* (1998) found that ALH84001 has extremely low Ni, Ir, Au, Re and Os compared with other Martian meteorites. From this data, they model an old Martian mantle, depleted in siderophile elements.

Gleason *et al.* (1997) found a significant difference in the trace element pattern for the "crushed" central zone from the bulk rock (figure X-25).



**Figure X-14.** Hydrogen isotopic ratio and water content as a function of temperature of release from ALH84001. This is figure 2 from Leshin et al. (1996), GCA **60**, 2640.



**Figure X-15.** Summary of <sup>53</sup>Cr-<sup>53</sup>Mn systematics in some solar system bodies. This is figure 1 from Lugmair et al. (1996).

# **Radiogenic Isotopes**

Ash et al. (1996) determined a shock age by <sup>39</sup>Ar/<sup>40</sup>Ar of  $4.0 \pm 0.1$  Ga based on the Ar released above  $400^{\circ}$ C. Their plateau age from maskelynite is 4.1 - 4.2 Ga (figure X-10a). Bogard and Garrison (1997) determined an apparent "plateau" age of  $4.29 \pm 0.06$ Ga, but argued that this is critically dependent on the type of Ar correction that is applied (figure X-10b). A "preferred" age of  $4.18 \pm 0.12$  Ga is calculated, based on the assumption that <sup>36</sup>Ar is terrestrial. Turner et al. (1997) determined an "average 39Ar/40Ar age" of about 3.92 Ga, but stated that the "true value lies somewhere between 4.05 Ga and 3.8 Ga" depending on the type of data correction that is chosen. Jagoutz et al. (1994) found that Sm-Nd isotope systematics for mineral separates fit a 4.56 Ga isochron (figure X-11). Nyquist et al. (1995) also found that both Rb-Sr and Sm-Nd isotope systems fit 4.56 Ga isochrons (figures X-12 and X-13), but that a Sm-Nd isochron defined by a "cleaned" pyroxene separate and several "whole rock" samples gave an age of 4.50 ± 0.13 Ga. Miura et al. (1995) also reported an old age of 3 - 4 Ga by K-Ar. Murty et al. (1995) calculated 3.74 Ga. Wadhwa and Lugmair (1996) reported an "age" based on Rb-Sr isochron through bulk rock and pyroxene separates of  $3.84 \pm 0.05$  Ga.

Wadhwa and Lugmair (1996) reported an "age of formation" of the carbonates in ALH84001 as  $1.39 \pm 0.1$  Ga, based on the Rb-Sr isochron through carbonates and maskelynite. Preliminary analyses by laser probe <sup>39</sup>Ar/<sup>40</sup>Ar of a single large carbonate/maskelynite grain gave an age of 3.6 Ga (Knott *et al.*, 1995). However, the age of the carbonates in ALH84001 has proven difficult to determine and remains uncertain (Turner *et al.*, 1997).

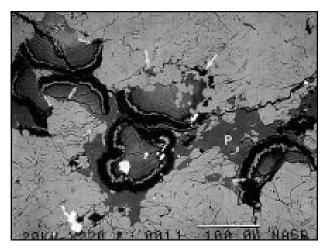


Figure X-16. Back-scattered-electron (BSE) photograph of thin section of ALH84001 illustrating several "orangettes" in cross section. This is figure clearly shows that the carbonate globules are replacing the maskelynite/plagioclase (P) in the sample. The bright, roughly circular features are Fe-rich zone containing magnetite and sulfide. This zone is surrounded by Mg-rich carbonate (dark in BSE) and a second, thin bright Fe-rich zone. The scale bar is 100 microns. This is figure 4 from Trieman (1994b), Meteoritics 30, 295.

### **Cosmogenic Isotopes and Exposure Ages**

Using  $^{14}$ C, Jull *et al.* (1989) originally determined the terrestrial age for ALH84001 as  $11.3 \pm 1.0$  thousand years, but later revised it to  $6.5 \pm 1.3$  thousand years (Jull *et al.*, 1994a). Nishiizumi *et al.* (1994) also reported  $6.5 \pm 1.0$  thousand years by  $^{14}$ C. Finally, after leaching experiments to separate carbon components, Jull *et al.* (1995) again recalculated the  $^{14}$ C exposure age as ~13 thousand years.

From cosmic-ray produced  ${}^{3}$ He,  ${}^{21}$ Ne and  ${}^{38}$ Ar, Eugster (1994) and Eugster *et al.* (1996, 1997) derived a cosmic-ray exposure age for ALH84001 of 15 Ma and concluded that ALH84001 was "*ejected from Mars well before any of the other Martian meteorites that have been collected so far.*" Miura *et al.* (1995) reported a cosmic ray exposure age of  $14.5 \pm 1.8$  Ma. Murty *et al.* (1995) measured the  ${}^{21}$ Ne exposure age as 16.4 Ma. Swindle *et al.* (1995b) determined an exposure age of  $15.8 \pm 1.6$  Ma. Bogard (1995) calculated an exposure age of 16 Ma from  ${}^{21}$ Ne data and 18 Ma from  ${}^{38}$ Ar data.

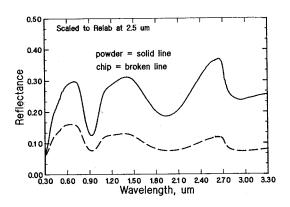
Score and Mittlefehldt (1993) reported the <sup>26</sup>Al activity to be 61±2 dpm/kg. Nishiizumi *et al.* (1994) studied the <sup>10</sup>Be and <sup>36</sup>Cl as a function of depth and concluded that ~3 cm was lost to ablation. By determining cosmic

ray tracks, Goswami *et al.* (1997) reported that ~5 cm was ablated.

# **Other Isotopes**

Oxygen isotopes, similar to those of SNC meteorites, were reported by Clayton (1993b) and Clayton and Mayeda (1996) (figure I-2). Romanek *et al.* (1996a) reported oxygen isotopes for maskelynite in ALH84001. Valley *et al.* (1997a, b), Leshin *et al.* (1997), Gilmour *et al.* (1997a, b), Saxton *et al.* (1997), Farquhar *et al.* (1998) and Eiler *et al.* (1998) have all found that oxygen isotopes in the carbonates in ALH84001 are enriched in <sup>18</sup>O and strongly zoned from core to rim, but these authors do not agree on the interpretation of the cause of this zoning. Baker *et al.* (1998) have reported the  $\delta$ <sup>18</sup>O for water released during heating steps.

Carbon and oxygen isotopes in  $CO_2$  released by acid dissolution from carbonates have been studied by Romanek *et al.* (1994a) who found that  $\delta^{13}C$  was +40 ‰ and  $\delta^{18}O$  was +20 ‰. During differential acid-



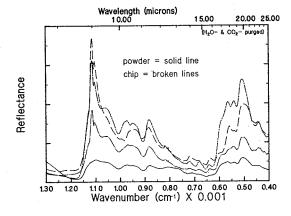


Figure X-17. VIS, NIR and mid-Ir reflectance spectra of ALH84001,92. This is figure 1 and 2 from abstract by Bishop et al. (1994), Meteoritics 29, 444.

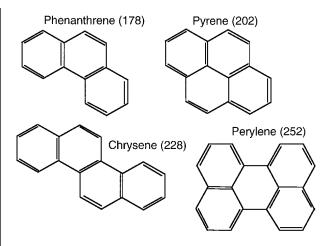


Figure X-18. Some of the polycyclic aromatic hydrocarbon compounds reported by McKay et al. (1996) in carbonate areas of ALH84001. The major peak was mass 228. The absence of other hydrocarbons is striking (see mass spectrum, figure 1 in McKay et al.).

etching of the carbonates in ALH84001, Jull *et al.* (1995, 1996b, 1997, 1998) found that the initial CO<sub>2</sub> released contained <sup>14</sup>C enrichment associated with light <sup>13</sup>C (figure I-14), but that the CO<sub>2</sub> released during later steps was low in <sup>14</sup>C and had the highest  $\delta^{13}$ C (+45 ‰). Grady *et al.* (1994a) and Leshin *et al.* (1996c) also reported heavy  $\delta^{13}$ C and  $\delta^{18}$ O for CO<sub>2</sub> released from ALH84001. Apparently the major carbonate phase in ALH84001 formed from the Martian hydrosphere/atmosphere (Jull *et al.*, 1996b, 1997a).

The D/H ratio of water released by heating steps was studied by Watson *et al.* (1994c) and Leshin *et al.* (1996c). She found  $\delta D$  for the highest temperature step to be +783 ‰, comparable to the values measured for the nakhlites (figure X-14) - *see also Nakhla.* This is less than the extreme  $\delta D$  found in the shergottites. Boctor *et al.* (1998a,b) have also reported  $\delta D$  +200 ‰ to +500 ‰ for phosphates and carbonates in ALH84001.

Miura and Sugiura (1994), Murty *et al.* (1995) and Grady *et al.* (1996a) reported heavy nitrogen isotopes released in high temperature steps. Murty and Mohapatra (1997) reported a component with  $\delta^{15}N > 47$  ‰. Murty *et al.* (1995) speculated that the lightest  $\delta^{15}N$  value of -21 ‰ might be the Martian indigenous component. However, Mathew and Marti (1998) found  $\delta^{15}N = -30$  ‰ in the low temperature release and concluded that the nitrogen released from the carbonate had not equilibrated with the Martian atmosphere ( $\delta^{15}N = 620$  ‰).

Table X-2. Thin sections of ALH84001 (52).

butt	section	1998	previous	parent	figure in
1				0	
,1	2	Mason		,0	Mason et al. 1992
	,3 ,5	Mikouchi	Danika		Mason et al. 1992
		Keil	Papike		
	,6* ,7		Berkley, McSween		
		Treiman	Hewins		
25	,8	Wadhwa	Prinz	1.4	
,25	27	Keil	Doubles	,14	
	,27		Berkley Shaw		
	,36 53*	MCC			S
	,53*	McSween	Warren, Mittlefehldt		Scott et al. 1997
<i>c</i> 1	,80*	Mittlefehldt	Capuano	0	
,61	60	MCC	Limochusta	,9	
	,62	MCC	Lipschutz		
	,63	Mikouchi	Shaw		NC 1 6 11 1/ 100 4
	,64	Friedmann	Mittlefehldt		Mittlefehldt 1994
	,81*	Capuano	Papike, Alexander		
	,225	Hofmann	Wadhwa		perglue
	,314	Greshake			perglue
	,315	Mojzsis			perglue
,66	02	)	N. 1. 6.1.1. 77	,0	1.400
	,82	MCC	Mittlefehldt, Kargel		McKay et al. 1997
	,83	Shearer	Yanai		
	,84*	Alexander	McSween, Meyer, Petaev		
	,226	Buseck	Wadhwa		perglue
,70				,0 crushed	
	,85	MCC	McSween		
	,86	Beauchamp	Mittlefehldt		
	,87	Shearer			
	,223	Bishop	Wadhwa		
,72				,0	
	,88*	Capuano	Mittlefehldt		
	,89	ElGoresy	Wlotzka, Keil		
	,140	Boynton			Gleason et al. 1997
,74				,0	
	,90	MCC	Mittlefehldt		
	,91*	Petaev	Stolper, Leshin, Prinz		
	,141	Koeberl			
,104				,69	
	,142	Treiman	Hofmann	sup	perglue
	,224	Kargel	Wadhwa		
,116				,69	
	,144	Mittlefehldt			

Table X-2. Thin sections of ALH84001 (52) continued.

butt	section	1998	previous	parent	figure in
,119				,69	
	,145	Mittlefehldt			superglue
	,146*	MCC	Prinz, Keil, Mittlefehldt		
	,307	Wadhwa			superglue
	,308	Blake			superglue
	,309	Buseck			superglue
	,310	Leshin			
	,311	Valley			
,120				,69	
	,143	Buseck	Hofmann		superglue
	,173	Keil	Snyder		
	,205	Fisk	Walker		
	,316	MCC			superglue
	,317	MCC			superglue
,153				,21	
	,168	Blake	McSween		
,247				,65	_
2.50	,313	Harvey		202	superglue
,268	201	**		,202	
	,301	Harvey			superglue
	,302	Harvey			superglue
	,303	Harvey			superglue
222	,312	Harvey		<i>(5</i>	superglue
,322	222	Dobbino		,65	
	,323	Robbins			

<sup>\* =</sup> used for rotation - see processing section

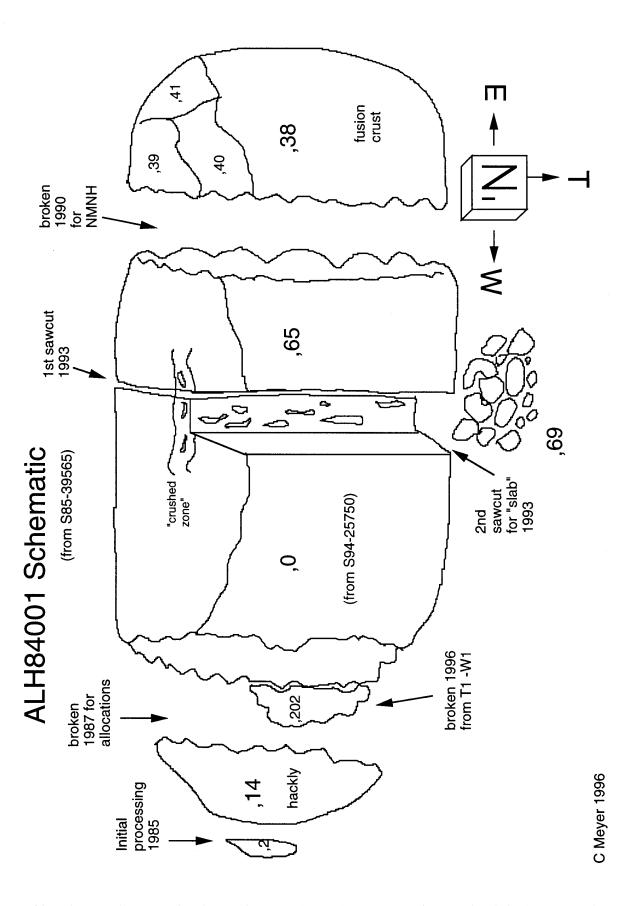
Miura *et al.* (1995), Murty *et al.* (1995), Murty and Mohapatra (1997) and Swindle *et al.* (1995b) found that ALH84001 contains high <sup>129</sup>Xe. However, Ash *et al.* (1996) found little evidence for the presence of a significant Martian atmosphere component in their piece. Gilmour *et al.* (1996) found that the excess <sup>129</sup>Xe was in the orthopyroxene and not in the carbonate.

Lugmair *et al.* (1996) studied the <sup>53</sup>Mn -<sup>53</sup>Cr systematics in mineral separates (chromite, pyroxene and bulk silicate) of ALH84001 and found that all splits gave the same <sup>53</sup>Cr/<sup>52</sup>Cr excess of  $0.22 \pm 0.10\epsilon$ , similar to data from Shergotty (figure X-15).

Shearer *et al.* (1996a, 1997) and Greenwood *et al.* (1997a, b) determined the isotopic composition of S in ALH84001 by the ion microprobe technique (figure X-24). They found greater fractionation of <sup>34</sup>S/<sup>32</sup>S in sulfide phases in ALH84001 "*than for any other meteorite*", but nothing like the effect that bacteria can produce. However, most of the pyrite grains studied by Shearer *et al.* (1996b, 1997) and/or Greenwood *et al.* (1997 a, b) were large grains (10-20 microns), and not the extremely fine-grained sulfides reported by McKay *et al.* (1996) (pyrrhotite/griegite?) in the black outer rims of the carbonates. Boctor *et al.* (1998) have also reported δS for pyrite in ALH84001.



**Figure X-19.** Photograph of ALH84001,1 and ,65 after it was sawn in 1994. The slab fell apart during cutting. Cube is 1 cm. (NASA # S94-25750) (See also figure X-20.)



**Figure X-20.** Schematic illustrating breaking and sawing of ALH84001 up to 1996. More detailed information is kept in the "data pack" maintained by Curator's Office at JSC.

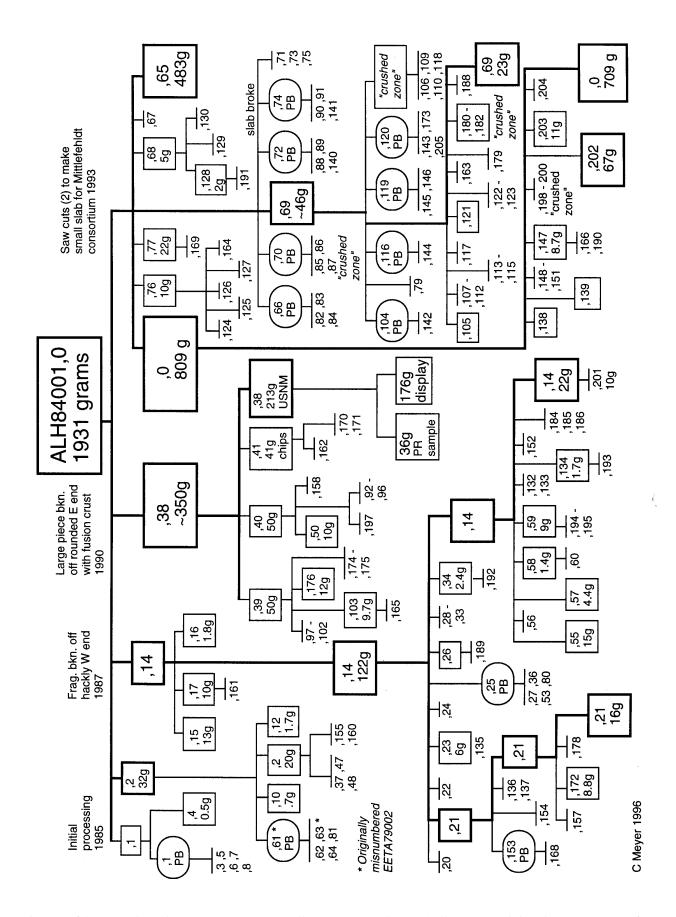


Figure X-21. Genealogy diagram for ALH84001 illustrating complexity of allocation and distribution up to 1996.

Compiler's note: Only specialized bacteria fractionate S; thus lack of fractionation of S isotopes does not mean lack of bacterial action.

# **Carbonate "Orangettes"**

Mason *et al.* (1992), Mittlefehldt (1994a) and Treiman (1995b) originally reported clusters of orange carbonates in thin sections of ALH84001 (figure X-16). These special features have variously been referred to as "orange spheroids" by Romanek *et al.* (1995), "carbonate globules" by McKay *et al.* (1996) and Scott *et al.* (1997), "rosettes" by Harvey and McSween (1995, 1996), "rounded zoned blebs" by Mittlefehldt (1997) and "disk-shaped concretions" by Valley *et al.* (1997).

Complier's note: Clearly, these special features require a unique name — so I proposed "Carbonate Orangettes" in the first edition of this compilation. However, the name has not caught on.

"Carbonate Orangettes" are only a very minor phase assemblage of ALH84001 (~0.5%). They occur as small (100 to 250 micron) concentric spheroids, in the interior of the igneous portions of the rock (Mittlefehldt, 1994a), in the "crushed zones" (Treiman, 1995b) and along natural fractures (McKay *et al.*, 1996) where they are apparently "pancake-like" (Romanek *et al.*, 1995). Typically, these carbonate "orangettes" are zoned, from Ca- and Fe-rich to Mg-rich (Harvey and McSween, 1995, 1996). They are also apparently zoned in Mn/Fe (Treiman, 1995b; McKay *et al.*, 1996).

Typically, each "orangette" has a fine-zoned, black-white-black, outer rim — as in an "Oreo cookie." The black outer zones (~1-5 microns) are Fe- and S-rich, while the white sandwich zone is nearly pure magnesite (Mittlefehldt, 1994a; Treiman, 1995b; Thomas *et al.*, 1996; McKay *et al.*, 1996). Magnesite has crystal faces projecting outward (Romanek *et al.*, 1994; McKay and Lofgren, 1997). The Fe-rich zones contain fine, single-domain, magnetite (Thomas *et al.*, 1996). In some cases, an additional zone of pure magnesite is found beyond the outer black zone. So, optically, the best preserved "orangettes" zone from dark orange to light orange, black, white, black, white.

Within one of the granular bands, Treiman (1995b) reported on a concentric, zoned carbonate patch, where the carbonate was found as a 3-dimensional, interconnecting, filling within a mesh of crushed orthopyroxene grains. The same compositional zoning

is present in this patch as in the case of other "orangettes." In other cases, the carbonate "orangettes" appear to be "growing" free on the surfaces in the freshly-broken, but pre-existing, natural fractures of the rock (McKay *et al.*, 1996). Some of the carbonate globules even appear "pancake-like", suggesting that the carbonates formed in the restricted width of a thin fracture (Romanek *et al.*, 1995; McKay *et al.*, 1996).

Romanek et al. (1995a) and Thomas et al. (1996) studied these fine-grained carbonate lithologies and observed that magnetite grains in the dark outer band showed "similarities to those formed as a byproduct of certain biological activities." Thomas et al. (1995) and McKay et al. (1996) have reported PAHs (polycyclic aromatic hydrocarbons) associated with these carbonate "orangettes." McKay et al. argued that "the carbonate globules are similar in texture and size to some terrestrial bacterially induced carbonate precipitates" (see section on "Biogenic Hypothesis").

The temperature of formation of these carbonate "orangettes" has been a focus of discussion. On the basis of major element analysis of the carbonates, and equilibrium phase relationship of carbonates, Mittlefehldt (1994a) and Harvey and McSween (1995, 1996) concluded the temperature of formation was on the order of 700°C. On the other hand, Romanek et al. (1995a), McKay et al. (1996) and Valley et al. (1997) have argued that oxygen isotope data indicate carbonate formation between 0 and 80°C. Valley et al. (1997), Saxton et al. (1997) and Leshin et al. (1997) have refuted the high temperature formation of carbonate with oxygen isotope data collected by ion microprobe. However, the arguments for the temperature of origin requires an assumption of equilibrium. In fact, the extensive chemical zoning and the complex fine-grained mineral assemblage of the outer rims clearly indicates that these "orangettes" did not form in an equilibrium environment (Romanek et al., 1995). Kirschvink et al. (1997) have used magnetic data to also show that their small pyroxene sample could not have been exposed to high temperature during the secondary event that produced the carbonate.

The nature of the metasomatism (or alteration) during the carbonate deposition (or replacement) has been another topic of discussion. Wadhwa and Crozaz (1994b, 1995b) introduced the idea of two stages of "infiltration metasomating fluids." Gleason et al. (1997) interpret the petrographic textures and chemical compositions to be consistent with "an inorganic origin for the carbonate, involving dissolution-replacement reactions between CO<sub>2</sub>-charged fluids and feldspathic glass" and "clearly postdated processes that last redistributed the REE in the meteorite". McKay et al. (1998) have been so bold as to propose that the very fine, set of "web-like" veins that they observed, was "precipitated from a fluid that permeated the granulated feldspathic zones" and that the various crack filling minerals in ALH84001 were deposited from "fluids of varying compositions" which "moved freely, leaving behind a variety of minerals as evidence of their passage."

Griffith and Shock (1995, 1997) have provided a useful discussion of hydrothermal carbonate formation on Mars based on theoretical calculations and their experience with Icelandic basalts. See also the discussion of alteration in Treiman (1995b), Wentworth and Gooding (1995) and Harvey and McSween (1995, 1996).

Complier's note: Although, water was apparently not involved with the CO<sub>2</sub> alteration of ALH84001, water would certainly have been needed for "biogenic activity"!!!

Two, different, shock-melting models for the origin for the carbonates in ALH84001 have been proposed (Harvey and McSween, 1996; Scott *et al.*, 1997). These models have the apparent advantage of not requiring fluids flowing through the rock, but they do imply a high temperature origin for the carbonates.

The time of formation of the carbonates in ALH84001 is also important to determine (see section on "Radiogenic Isotopes"). The initial "age" of ~3.6 Ga (Knott et al., 1995; used by McKay et al., 1996) has been withdrawn (Turner et al., 1997), because the laser spot included some plagioclase. Wadhwa and Lugmair (1996) determined an age of 1.36 Ga. Kring et al. (1997, 1998) and McKay et al. (1997) have attempted to establish the relative ages of maskelynite and carbonate formation using the textural relations and attempts to determine the age of the maskelynite have been made (Bogard and Garrison, 1997; Turner et al., 1997). However, more work is still required to solve the important problem of the time of carbonate formation.

### **Isotopic Results on Carbonate "Orangettes"**

•	δ <sup>13</sup> C	δ <sup>18</sup> O	<sup>14</sup> C
magnesite rims			
Valley et al. 1997a		20.6±1.3‰	
Saxton <i>et al.</i> 1997		20-22‰	
cores			
Valley et al. 1997a	46±8‰	16.7±1.2‰	
-		11.5±2.0‰	
Saxton et al. 1997		10-22‰	
Leshin et al. 1997		6-22‰	
Farquhar et al. 1998		18.3‰	
•			
bulk			
(acid dissolution)			
Jull et al. 1997a	32-40‰	10-17‰	high
			activity
Grady et al. 1994a	40.1‰		•
other authors*	36±10‰	17.5±2.7%	0
bulk			
(stepped combustion)			
Jull et al. 1998 (low temp.)	-2233‰		37-52%
• • •			modern
Jull et al. 1998 (high temp.)	32-40‰		<3%
			modern

<sup>\*</sup> averages quoted by Valley et al.

Eiler *et al.* (1998) have studied the correlation of oxygen isotopes with variation in major element composition of the carbonates (zoning).

# **Other Experiments**

Natural thermoluminescence was reported as  $1.3\pm0.1$  krad (Score and Mittlefehldt, 1993). Bishop *et al.* (1994) and Bishop and Pieters (1996) have measured the infrared reflectance spectra from ALH84001 (figure X-17). Sinha and Goswami (1994) and Goswami *et al.* (1997) studied nuclear tracks from numerous splits of ALH84001 and concluded that it lost 5 cm on all sides due to ablation in the Earth's atmosphere. Hence the ALH84001 specimen was a single fall.

Kirschvink et al. (1997) and Collinson (1997) reported on magnetic studies of ALH84001. Kirschvink et al. found that "two adjacent grains of pyroxene each possessed a stable natural remanent magnetization, implying that Mars had a substantial magnetic field when the grains cooled." Collinson was not able to determine which mineral was responsible for the recorded magnetism.

Becker *et al.* (1997) and Clemett *et al.* (1998) have performed experiments to show whether polycyclic aromatic hydrocarbons (naphthalene) can be selectively adsorbed and concentrated on carbonates.

The study of ALH84001 can be expected to lead to studies of some selected terrestrial rocks with apparently similar features. For example, Treiman *et al.* (1998) have found similarities of carbonates in mantle xenoliths and their host basalts from Spitsbergen with some of the features in ALH84001. Thomas-Keprta *et al.* (1998) are also studying the bacteria from the Columbia River Basalts.

Jones and Schwandt (1998) have been performing experiments related to the high pressure, high temperature stability of siderite. Bell *et al.* (1998) and Schwandt *et al.* (1998) have attempted to determine whether shock melting of carbonate can occur.

#### **Organics**

Grady et al. (1994a) reported 257.2 ppm "organics" released at a temperature below 450°C. They found these "organics" to have  $\delta^{13}C = -21.5$  %. This was confirmed by Jull et al. (1998) who find that at least 80% of the combustable "organic" material in ALH84001 is terrestrial contamination (i.e. contains <sup>14</sup>C). Thomas *et al.* (1995) and McKay *et al.* (1996) reported unique polycyclic aromatic hydrocarbons (PAHs) located on fresh fractures in ALH84001 that also contain the carbonate "orangettes." McKay et al. (1996) give evidence that these PAHs are not like any known terrestrial or meteoritic contamination (figure X-18). However, only one mass spectrum was presented (figure 1 in McKay et al., 1996). Becker et al. (1997) argued that the mass spectrum for PAHs in EETA 79001 were roughly similar. Using TOF-SIMs, Stephan et al. (1998a,b) studied PAHs on fractured surfaces where carbonates are located in ALH84001 (figure X-28). This technique has higher spatial resolution that that used by McKay et al. (1996) allowing Stephan et al. to conclude that the PAHs were not associated with the carbonates, as had been asserted by McKay et al. On the other hand, using STXM and FTIR techniques with narrow spatial resolution, Flynn et al. (1998a,b) reported close spatial association of organics with carbonate globules and rims in ALH84001.

Bada *et al.* (1998) detected trace amounts of amino acids (glycine, serine and alanine) in the carbonate component of ALH84001 using high performance liquid chromatography. The detected alanine consists primarily of the L-enantiomer; a strong indication that the amino acids found in this rock are the result of

terrestrial contamination. (Presumably, amino acids from Mars would be so old and highly shocked that they should be both right and left handed).

Jull et al. (1998) provided isotopic evidence (see table above) for a terrestrial source of most of the organic compounds found in ALH84001 (as well as in EETA79001). They also reported a hint of a small pre-terrestrial carbon component of unknown origin (possibly the residual acid-insoluble or refractory organic phase).

### **Biogenic Hypothesis**

In their landmark paper on ALH84001, McKay *et al.* (1996) made the following observations:

- 1) ALH84001 is an igneous rock from Mars "that was penetrated by a fluid along fractures and pore spaces, which then became the sites of secondary mineral formation and possible biogenic activity."
- 2) the formation age for the carbonate globules "is apparently younger than age of the igneous rock."
- 3) high resolution SEM images reveal minute features "resembling terrestrial microorganisms, terrestrial biogenic carbonate structures, or microfossils." (images can be viewed at http://rsd.gsfc.nasa.gov/marslife)
- 4) co-occurrence of both oxidized magnetite and reduced sulfide particles "that could have resulted from oxidation and reduction reactions known to be important in terrestrial microbial systems" in the outer margins of the carbonate, which appears to be in dissolution.
- 5) the "presence of organic matter (PAHs) associated on surfaces rich in carbonate deposits."

McKay et al. cautiously admitted that while "none of these observations is in itself conclusive for the existence of past life," that when considered collectively, particularly in view of their spatial association, provided "evidence for primitive life on early Mars." However, Anders (1996) and McSween (1996) provided arguments for an inorganic origin for each of these features. Bradley et al. (1997) and McKay et al. (1997) have argued about whether or not the "microfossil features" could be artifacts of the

SEM techniques used and/or exsolution features exposed at mineral edges. Browning and Broucier (1997) argued that calcite, magnesite and pyrrhotite can coexist over a wide range of conditions

Gibson et al. (1997a) reported "the 'nanobacteria'-like features within ALH84001 range in size from 20 to 500 nanometers. The structures are spherical, elongated, and segmented in shape and several appear to be dividing." McKay et al. (1997) and Steele et al. (1997) also documented the occurrence of "biofilms" within ALH84001 associated with the carbonates. Valley et al. (1997a, b) and Kirschvink et al. (1997a, b) provided further evidence of low temperature formation of the carbonates in ALH84001 - which is a necessary condition for biogenic activity.

McSween (1996) discussed the evidence of McKay et al. for "possible relic biogenic activity in Martian meteorite ALH84001." Other studies, for and against the "biogenic hypothesis", have been reported; including Leshin et al., Bradley et al., Thomas-Keprta et al., Shearer et al., Wright et al., Gilmour et al., Greenwood et al., and others (all 1997). Gibson et al. (1997a, b, d) provided summaries of the evidence for "biogenic activity" in the carbonates in ALH84001. However, the work of Jull et al. (1998); Bada et al. (1998) and Farquhar et al. (1998) cast considerable doubt on the "biogenic hypothesis."

Compiler's note: Allan Treiman maintains a really useful website on the evidence for and against past biogenic activity (?) in ALH84001 at:

http://cass.jsc.nasa.gov/lpi/meteorites/ mars\_meteorite.html

#### **Processing**

The initial processing of ALH84001 (1985) was from the angular hackly end, where a piece (,2) was broken off for preliminary allocations. Additional allocations were made in 1987 from a larger piece (,14), also from this hackly end. In 1990, a large piece (,38) with intact fusion crust was split off the smooth, blocky end (with rock-splitter) for display (as a diogenite) at the Smithsonian (USNM). In 1994, in an attempt to saw a slab out of the middle of the main sample for a consortium study led by Duck Mittlefehldt, the small slab broke at a "porous band of weakness" halfway through (figure X-19). The "half slab" (,69) broke

into many pieces, from which the consortium allocations were made.

In August 1996, allocations of ALH84001 were halted until NASA and NSF proposals were reviewed and a new clean processing cabinet prepared. In March 1997, a special Mars Meteorite Working Group (M-MWG) committee considered 45 sample requests. The committee decided to preserve ALH84001,0 (about 709 grams) for future studies, but allowed disaggregation of ,65 (about 483 grams) for allocation along with the smaller pieces (Marvin, 1997). Scientists received this second round of allocations of ALH84001 in June-July 1997. In 1997, numerous, small, oriented samples were taken for magnetic orientation.

Figures X-20, X-21 and X-26 attempt to diagram the complex processing for this sample. Table X-2 shows the sequence for the 51 thin sections that have been distributed as of January 1998. These fifty-one sections are derived from 14 different chips (some were prepared with superglue for easy detachment for TEM studies). Obviously, different scientists have been studying different portions of this rock. To partially solve this problem, 8 thin sections were used for rotation among petrographers (1 month each) during 1997-8 (Table X-2).

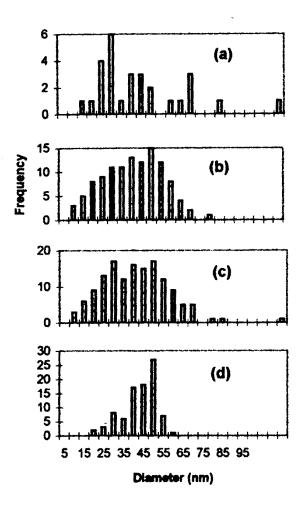


Figure X-23. The distribution of particle diameters for magnetite crystals from: (a) the interior of the ALH84001 carbonate globule without a rim, (b) the rim region of the ALH84001 carbonate globule, (c) the whole carbonate globule in ALH84001, and (d) bacterial magnetite from strain MS-1. This figure is from Golden et al. (1997) LPSC XXVIII, 428.

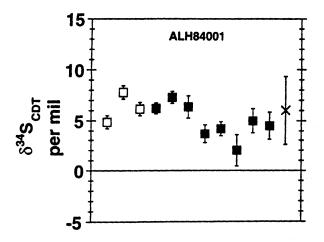


Figure X-24. Sulfur isotopic analyses of sulfides in ALH84001. Open symbols are from Shearer et al. (1996), black squares are from Greenwood et al. (1997) and X is for the black rims of the carbonates. This is figure 2 from Greenwood et al. GCA 61, 4449.

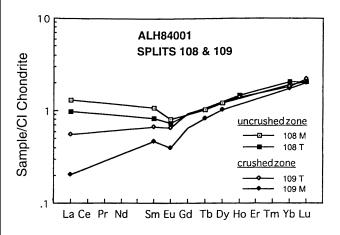


Figure X-25. REE patterns for samples of "crushed zone" compared with other subsamples of ALH84001. This is figure 7 from Gleason et al. (1997) GCA 61, 3511.

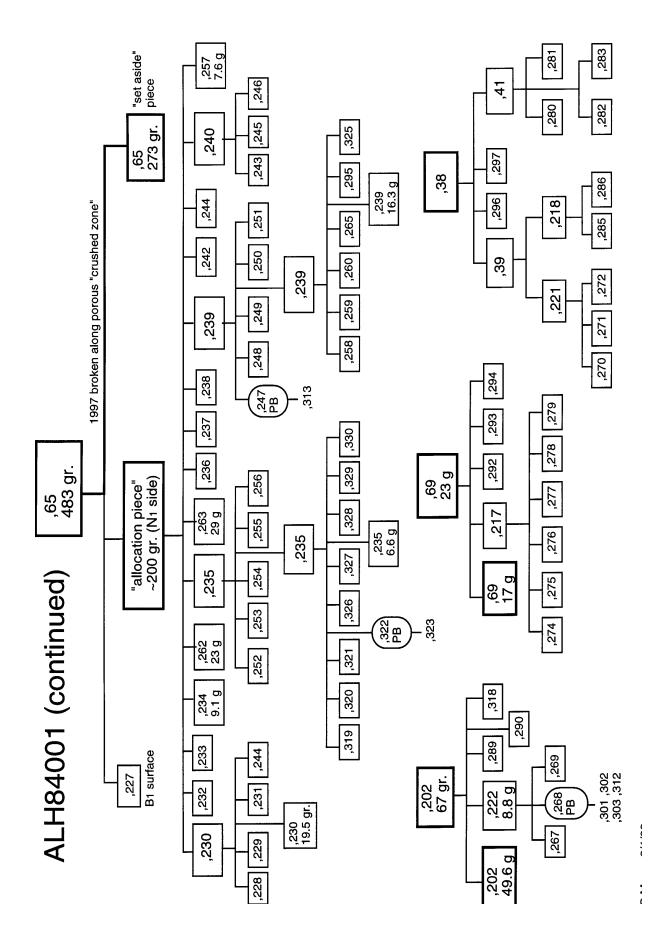


Figure X-26. Genealogy diagrams for 1997 processing of ALH84001 (as of Jan 1998).

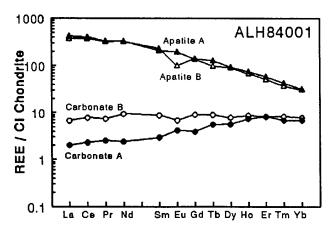


Figure X-27. REE patterns for apatites and carbonates in ALH84001 as determined by ion microprobe analysis. This figure is from Wadhwa and Crozaz (1995b) LPSC XXVI, 1452.

